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Derivation of Site-Specific Water Quality Criteria for Cadmium and the St. Louis River Basin, Duluth, Minnesota

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DERIVATION OF SITE-SPECIFIC WATER QUALITY CRITERIA FOR CADMIUM AND THE ST. LOUIS RIVER BASIN, DULUTH, MINNESOTA

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16. ABSTRACT

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The site-specific, maximum concentration derived from the recalculation procedure was slightly lower (1.3 as compared to 2.2 µg/l) than the national criterion value. The maximum concentration derived from the indicator species procedure was 7.0 µg/l and was calculated by using a water effect ratio from tests conducted in both site and laboratory water. Acute tests with several species demonstrated that cadmium was less toxic in site water than in laboratory water. The site-specific, maximum concentration derived from the resident species procedure (from eight species exposed to cadmium in site water) was 1.9 µg/l. The 30-day average concentrations were the same as the maximum concentrations in all procedures where the national acute-chronic ratio was used in the calculation. These concentrations were much lower when the site-specific, acute-chronic ratio was applied.

Acute tests conducted monthly in site water showed that cadmium toxicity varied by more than a factor of three over the year. This indicates the need for considering seasonal changes in physical and chemical characteristics of the site water when deriving criteria to protect aquatic life.

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TABLE OF CONTENTS

SECTION	PAGE
INTRODUCTION	1
Study site	2
PRODECURES AND TEST METHODS	
Procedures for calculating criteria	8
Water characteristics	9
Exposure systems	10
Toxicant solution	10
Biological procedures	11
Statistical analysis	14
RESULTS	15
DISCUSSION	24
CRITERIA CALCULATION	
Recalculation procedure	26
Indicator species procedure	27
Resident species procedure	31
Summary of criteria calculations	32
OVERALL ASSESSMENT	34
ACKNOWLEDGEMENTS	35
REFERENCES	36
APPENDIX A. Biological survey of aquatic species resident to the St. Louis River and river basin.	40
APPENDIX B. Ambient water quality parameters obtained for the St. Louis River site at Cloquet, Minnesota during the months of April through December 1981	45
APPENDIX C. Recalculation Procedure. Minimum data set for cadmium from the national criterion document for species and families resident to the St. Louis River	46
APPENDIX D. Indicator Species Procedure. Acute values (LC50) for indicator species exposed to cadmium in St. Louis River and reconstituted water	48

APPENDIX E. Acute (LC50) and chronic values for aquatic organisms exposed to cadmium in St. Louis River water. 49

APPENDIX F. Chronic toxicity values of two species exposed to cadmium in St. Louis River and Lake Superior water 50

APPENDIX G. Resident Species Procedure. Minimum data set of resident aquatic species exposed to cadmium in St. Louis River water. 51

APPENDIX H. Cadmium water quality criteria derived from the national and site specific procedures 52

LIST OF TABLES

TABLE		PAGE
1	Size, temperature, and source of aquatic species exposed to cadmium in St. Louis River and reconstituted water	12
2	Monthly averages in water quality parameters for cadmium tests conducted in St. Louis River, reconstituted and Lake Superior water.	16
3	Correlation coefficients for St. Louis River cadmium toxicity tests with fathead minnows and corresponding water quality parameters for the months April through December 1981.	18
4	Acute values (LC50, µg/l) for aquatic species exposed to cadmium in St. Louis River and reconstituted water	20
5	Survival and growth of fathead minnows exposed to various concentrations of cadmium in St. Louis River water for 32 days	21
6	Survival and young production of Ceriodaphnia reticulata exposed to various cadmium concentrations in St. Louis River water for 9 days	23

LIST OF FIGURES

FIGURE		PAGE
1	St. Louis River Basin	4
2	Duluth and Superior Estuary	5
3	St. Louis River site at the State Highway 33 crossing in Cloquet, Minnesota	7
4	Monthly LC50 values (± 95% confidence limits) for tests with one-day-old fathead minnows exposed to cadmium in St. Louis River and reconstituted water	17

ABSTRACT

Several freshwater aquatic species were exposed to cadmium in site and laboratory water to evaluate an "organism testing" protocol proposed by the U.S. Environmental Protection Agency for deriving site-specific, water quality criteria. The procedures of recalculation, indicator species, and resident species were used in this protocol to modify the national maximum and 30-day average cadmium criteria. These procedures were used to account for differences in species sensitivity and in the biological availability and/or toxicity of cadmium due to physical and/or chemical characteristics of the site water.

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Acute tests conducted monthly in site water showed that cadmium toxicity varied by more than a factor of three over the year. This indicates the need for considering seasonal changes in physical and chemical characteristics of the site water when deriving criteria to protect aquatic life.

INTRODUCTION

Under the Clean Water Act of 1977 [Sec. 304(a)(1)] the U.S. Environmental Protection Agency (U.S. EPA) is required to review and publish criteria for water quality necessary to protect public water supplies and the propagation of shellfish, fish and wildlife. Criteria present scientific data and guidance on the environmental effects of pollutants which can be useful to derive water quality-based regulatory requirements such as effluent limitations, water quality standards or toxic pollutant effluent standards (U.S. EPA, 1980a).

National water quality criteria have been derived by applying a set of guidelines (U.S. EPA, 1983a) to data for certain pollutants designated as toxic under Section 307(a)(1) of the Clean Water Act of 1977 persuant to an agreement in the case of Natural Resourses Defense Council et al. vs. Train, 1976. These guidelines specify that criteria should be based on an array of data from species, both plant and animal, occupying various trophic levels. Based on these data, criteria can be derived which should adequately protect the type of species necessary to support an aquatic community. Although criteria represent a reasonable estimate of pollutant concentrations consistent with the maintainance of designated uses, each state may appropriately modify these values to reflect local conditions.

Since national criteria may be either underprotective or overprotective, the Office of Research and Development and the Office of Water Regulations and Standards of U.S. EPA are currently developing guidelines (U.S. EPA, 1983b) for modifying national water quality criteria to local conditions or to site-specific criteria. National criteria are based on information obtained from toxicity and bioconcentration tests conducted in laboratory sources of water. However, toxicological information obtained for laboratory

tested aquatic species, however, may not be applicable to species in specific water bodies because: 1) the species at a particular site may be more or less sensitive than those included in the national criteria data base or 2) the physical and/or chemical charateristics of the water at the site may alter the biological availability and/or toxicity of the material.

The main purpose of this research was to test procedures that might be useful for deriving site-specific water quality criteria. The specific objective of the study was to conduct tests to evaluate an "organism testing" protocol for deriving site-specific criteria utilizing toxicity tests with several species of aquatic organisms in site and laboratory water. The type of tests and/or exercises that were performed in this study were designed to correlate with the site-specific guidelines as they are now proposed (U.S. EPA, 1983b). This study was designed to help identify problems that one might encounter when using the guidelines and to provide an example for a site-specific criteria derivation for a chemical at an actual site.

Tests were conducted with cadmium because this chemical is highly toxic to aquatic organisms (National Academy of Sciences, 1973), it is commonly found in the environment due to its presence in treated municipal wastes (U.S. EPA, 1980b), and its chemistry in water is such that it may be influenced by changes in water quality (Giesy et al. 1977; Calamari et al. 1980; Reid and McDuffie, 1981), which would be a major consideration for modifying the present national criteria.

Study site

The St. Louis River system near Duluth, Minnesota was chosen as the site for study because: 1) Water quality monitoring data and hydrodynamic and water quality models were available (DeVore, 1983). 2) It provided both clean and dirty water characteristics needed for biological testing and for

deriving a site-specific water quality criteria. 3) Resident aquatic species for this river system were already known (State of Minnesota, 1941; National Biocentric Inc. 1973; University of Wisconsin, 1976; DeVore, 1978; State of Wisconsin, 1982; U.S. EPA, 1983c; Mary Balcer, personal communication) (Appendix A).

The St. Louis River basin is a large area totaling 3,584 square miles in northeastern Minnesota (Figure 1) (Waters, 1977). It is located primarily in southern St. Louis County with small portions in adjoining counties and in Douglas County, Wisconsin. The St. Louis River system includes approximately 1,400 miles of streams, 815 miles of which are the St. Louis River and its tributaries (State of Minnesota, 1941). From source to mouth, the St. Louis River has a total length of 164 miles, flows in a general northeast-southwest direction and forms a drainage pattern roughly parallel to the north shore of Lake Superior. Nearly all water received by the St. Louis River is from surface drainage, bog seepage and overflow from lakes. Bog drainage and high humic content give the river its brown color. The water of the St. Louis River system is of moderate chemical fertility.

The mouth of the St. Louis River is an estuary containing approximately 11,500 acres of water. It has been developed into a major industrial port which serves as the economic base for the cities of Duluth, Minnesota and Superior, Wisconsin (Figure 2). Dredging and the discharge of municipal sewage, paper mill waste, wash water and other industrial wastes have degraded water quality in the St. Louis River below Cloquet, Minnesota since the turn of the century. Since 1979, however, domestic as well as industrial wastes from Duluth and the surrounding communities have been treated by the Western Lake Superior Sanitary District Treatment Plant (WLSSD). This has greatly improved water quality in a very short period of time. The WLSSD

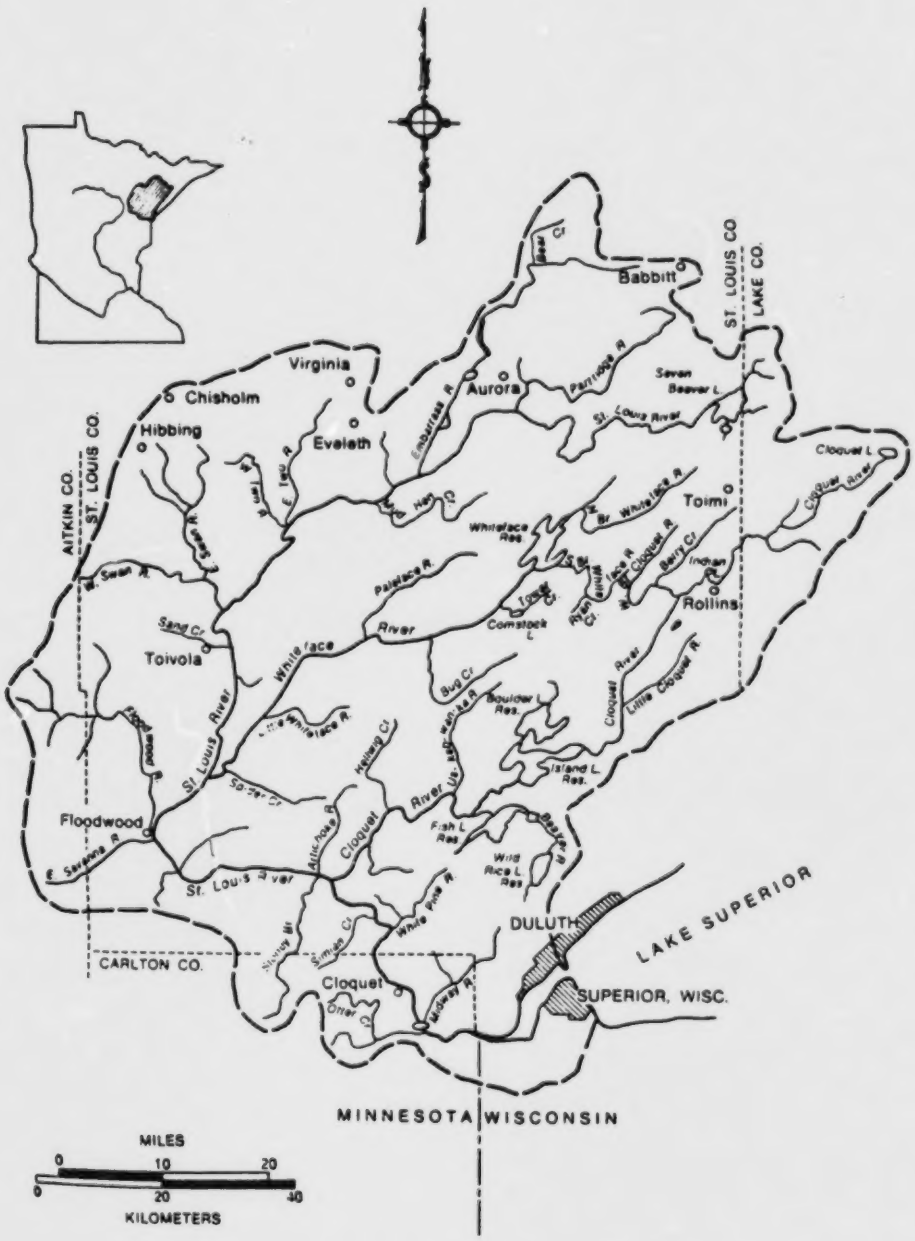

Figure 1. St. Louis River Basin (Waters, 1977).

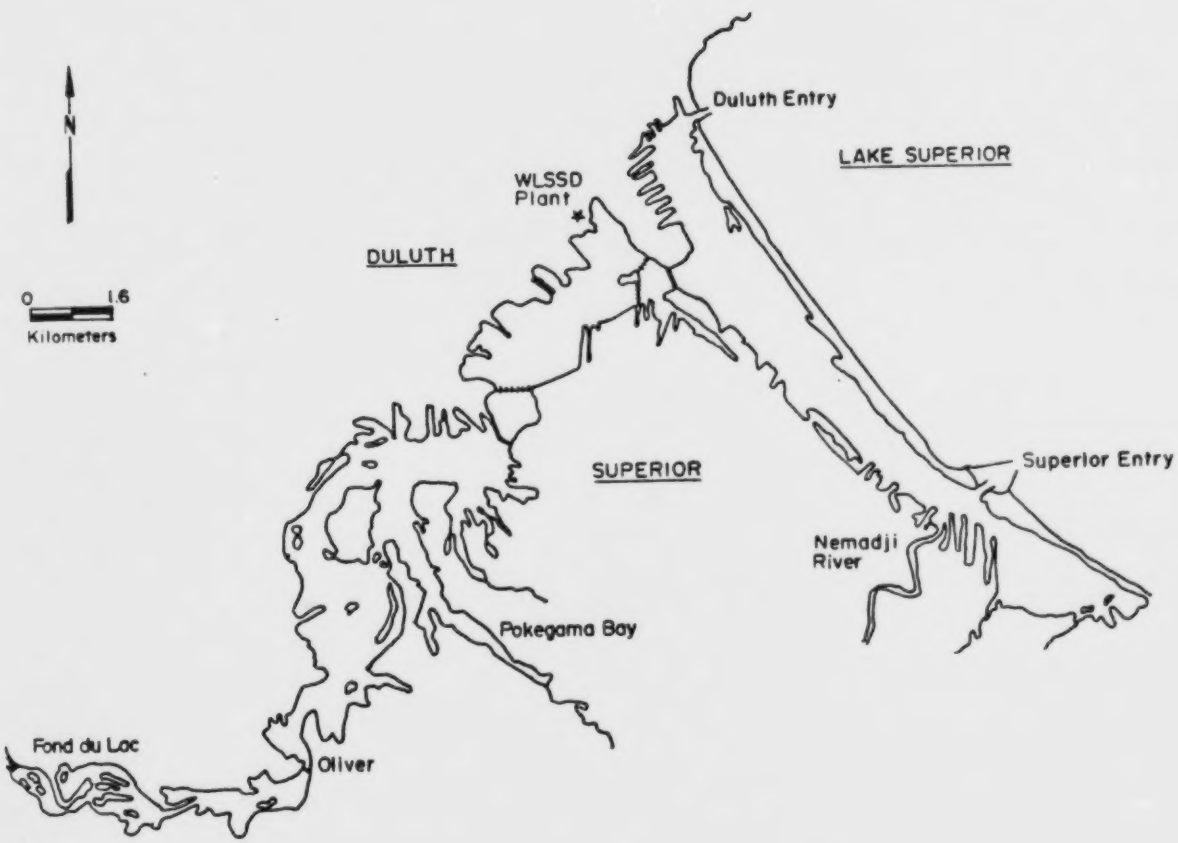

Figure 2. Duluth and Superior estuary.

plant treats an average of 160 million liters per day and removes over 300 metric tons of pollutants per day (Ducette, 1980). The effluent from this treatment plant is discharged into the estuary (Figure 2) and is the major point discharge of treated waste in this area.

The site chosen for a source of dilution water in this study was located approximately 34 miles upstream from the mouth of the Duluth-Superior estuary at the State Highway 33 crossing in the city of Cloquet, Minnesota (Figure 3). Water samples were taken from the north channel to represent the river's quality immediately before the influence of the Cloquet area. This site on the river was considered to have the highest water quality closest to the impacted Duluth-Superior estuary (Western Lake Superior Sanitary District, personal communication). Water at this site was also judged to be of high quality because several species of aquatic organisms were able to survive, grow and reproduce in it under laboratory conditions with no apparent adverse effects. No industrial point discharges existed upstream of this site. Ambient water quality parameters including metal analyses for this site obtained during the tests (from April to December 1981) are included in Appendix B.

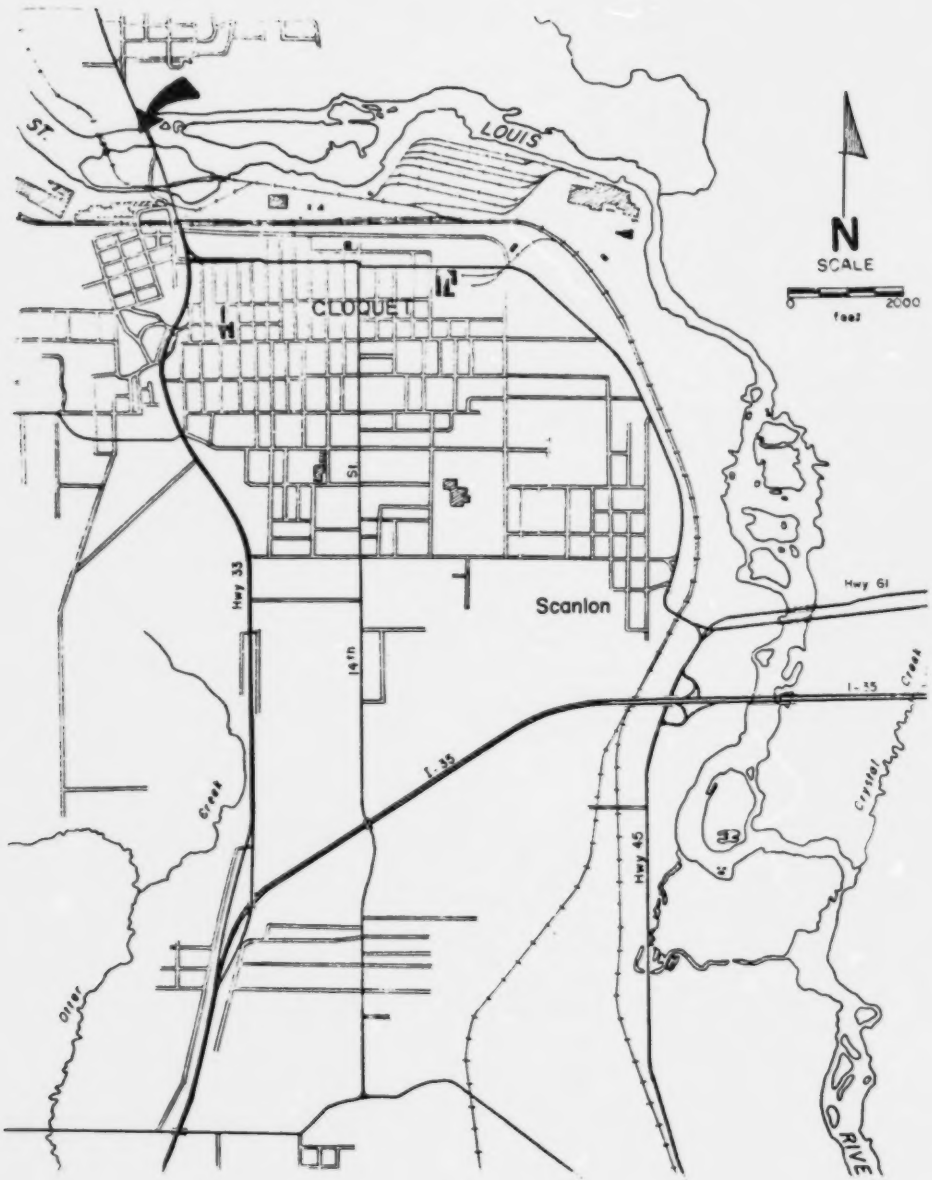

Figure 3. St. Louis River site at the State Highway 33 crossing in Cloquet, Minnesota.

PROCEDURES AND TEST METHODS

Procedures for calculating criteria

Three procedures were used in this study to modify the national maximum and 30-day average concentration criteria for cadmium. They were used for illustrative purposes only because all three procedures would not necessarily be used in an actual site modification. In addition, procedures to determine a Final Residue Value or a Final Plant Value (which are required in the National Guidelines for deriving water quality criteria; U.S. EPA, 1983a) were not included in this study because cadmium is not a lipid-soluble material and plants have not been shown to be as sensitive to cadmium as aquatic animals. Thus, the site-specific, Final Chronic Value for cadmium was the same as the site-specific, 30-day average concentration for all procedures conducted in this study.

The three procedures used to calculate a site-specific, criteria for cadmium in the St. Louis River were as follows:

1) the recalculation procedure was used to account for differences in cadmium sensitivity between species resident in the St. Louis River and those species contained in the national cadmium criteria document (U.S. EPA, 1983d). 2) The indicator species procedure was used to account for differences in the biological availability and/or toxicity of cadmium due to physical and/or chemical characteristics of the St. Louis River water and laboratory water by deriving a water effect ratio (toxicity in site water divided by the toxicity in laboratory water). 3) The resident species procedure was used to account simultaneously for differences in both resident species sensitivity and differences that may be attributed to water quality.

In addition to the above procedures, acute tests were conducted monthly on one-day-old fathead minnows to determine if seasonal changes in water quality affected the toxicity of cadmium in the St. Louis River.

A detailed description of defining a site, the rationale, assumptions and limitations of the site-specific procedures and their relationship to those used for deriving national water quality criteria are included in the proposed site-specific guidelines (U.S. EPA, 1983b).

Water characteristics

Water samples for preliminary and acute toxicity tests in St. Louis River water were taken below the water surface with 19 liter polyethylene jugs and immediately brought back to the laboratory for testing. Large quantities of water needed for chronic tests were obtained by pumping river water through a 30 meter, 5 cm diameter collapsible PVC hose to a 3,800 liter steel truck tank. Site water was then transferred to the laboratory and pumped into two 1,900 liter Teflon coated head tanks where it was stored and vigorously aerated prior to use. Both reconstituted and Lake Superior water were used as laboratory dilution water in comparative toxicity tests. Reconstituted water was made according to procedures described by the American Society for Testing and Materials (ASTM, 1980) for soft water. Unfiltered Lake Superior water was obtained directly from Lake Superior. Both waters were heated (if necessary) to the appropriate test temperature for each test.

Chemical characteristics of the site water were determined after each collection by the Western Lake Superior Sanitary District located in Duluth, Minnesota. In addition, chemical characteristics for all dilution waters were measured just prior to or during all toxicity tests at the Environmental

Research Laboratory, Duluth, Minnesota and were conducted according to procedures of the American Public Health Association et al. (1980).

Exposure systems

Static tests with larval fish were conducted in 600 ml glass beakers containing 500 ml of solution. Glass beakers containing 200 ml of solution were used for static tests with invertebrates. Wide mouth glass jars containing five to 10 liters of test solution were used for static tests with juvenile fish. Duplicate test chambers were used in all tests for each of five toxicant concentrations and a control. All test chambers used for these tests were contained in a water bath for temperature control. Fluorescent light bulbs provided a light intensity of 80 to 100 lux during a 16-h photoperiod.

Flow-through acute and chronic exposures with fish were conducted using a diluter system (Benoit et al. 1982) which delivered five toxicant concentrations and a control to four replicate chambers per treatment. Glass test chambers measured 7 cm wide x 19 cm long x 9 cm high with a water depth of 4.5 cm. The flow to each chamber was 12.5 $\pm$ 1 ml/min. Fluorescent bulbs provided a light intensity of 200 to 500 lux at the water surface during a 16-h photoperiod.

Toxicant solution

Stock solutions for static tests were prepared by dissolving reagent grade cadmium chloride ($CdCl_2$) in distilled water. After test concentrations were calculated, measured amounts of stock solution were diluted with the dilution water to provide for various toxicant concentrations. For flow-through tests, cadmium stock was dissolved in 19 liters of distilled water and pumped to the diluter via a fluid metering pump to produce the desired test concentrations. Water samples from each test

concentration and control were collected in 250 ml Nalgene LPE bottles at the beginning of each acute static test and once a week during flow-through tests. They were acidified with concentrated nitric acid (0.5% v/v) for analyses. Preliminary analysis indicated that no metal was lost in the water after 96 hours, therefore, water measurements for cadmium were made only at the beginning of the tests. Water samples were analyzed with a Perkin Elmer atomic absorption spectrophotometer equipped with either a HGA 500 graphite furnace or an automatic burner control. All measurements are expressed as total cadmium and not as the compound. The limits of detection for these procedures were ~0.25 and ~35 µg/l, respectively. To verify the accuracy of the method of analysis, known amounts of the metal were added to control water to obtain percentage recoveries. Percentage recoveries ranged from 91 to 110% for 76 spiked samples. In addition, one set of samples was periodically filtered through a 0.45 µ millipore filter to characterize the portion of dissolved metal. The mean percentages, standard deviation and number of samples of dissolved cadmium for individual tests (including five cadmium concentrations per test) were 84 $\pm$ 1.0 (8), 84 $\pm$ 1.0 (4), 96 $\pm$ 2.0 (9) for St. Louis River, Lake Superior and reconstituted water, respectively.

Biological procedures

Size, temperature and source of aquatic species exposed to cadmium in the St. Louis River and reconstituted water are shown in Table 1. Tests to determine a water effect ratio were conducted in both waters with each species at the same time and under the same test conditions. Tests with different species were conducted throughout the year as they became available from their respective sources. Procedures for conducting acute tests

Table 1. Size, temperature, and source of aquatic species exposed to cadmium in St. Louis River, and reconstituted water.

Species	Life Stage	Age(d) or Weight(g)	Test Temp.(°C)	Source
Cladoceran, (Daphnia magna)	Young	<1-d	20	Environmental Research Laboratory, Duluth, MN
Cladoceran, (Simocephalus vetulus)	Young	<1-d	20	"
Cladoceran, (Simocephalus serrulatus)	Young	<1-d	20	"
Cladoceran, (Ceriodaphnia reticulata)	Young	<1-d	22	"
Amphipod, (Gammarus pseudolimnaeus)	Juvenile	~0.1g	17	Eau Claire River Gordon, WI
Amphipod, (Hyalella azteca)	Juvenile	~0.0006g	7	St. Louis River Cloquet, MN
Mayfly, (Paraleptophlebia praepedita)	Nymph	~0.002g	12	"
Rainbow trout, (Salmo gairdneri)	Juvenile	0.4-0.6g	12	U.S. Fish and Wildlife Service
Brown trout, (Salmo trutta)	Juvenile	1.0-1.5g	12	"
Fathead minnow, (Pimephales promelas)	Embryo	<1-d	25	Environmental Research Laboratory Duluth, MN
	Larvae	<1-d	25	
	Juvenile	30-d	25	
Channel catfish, (Ictalurus punctatus)	Juvenile	0.6-0.7g	17	U.S. Fish and Wildlife Service
Bluegill, (Lepomis macrochirus)	Juvenile	0.2-0.6g	17	"

followed those described by the American Society for Testing and Materials (ASTM, 1980).

Tests were conducted monthly beginning in April and ending in December 1981 to determine the effect of seasonality on the physical and chemical characteristics of the site water and the subsequent effects on biological availability and/or toxicity of cadmium on fathead minnows. These tests were initiated by incubating fathead minnow embryos that were <24 hours old in St. Louis River water, reconstituted and/or Lake Superior water for four to five days, or until they hatched. Ten one-day-old larvae were then transferred to each dupliate test chamber and exposed for 96 hours for the calculation of LC50 values. Other acute tests with juvenile animals were initiated by first acclimating each species in site or laboratory dilution water at the test temperature for at least two days prior to testing. All cladocerans were reared in the dilution water for a sufficient amount of time to produce young before being tested. After acclimation, 10 or 20 animals of each species were transferred to each test concentration and control. Acute tests lasted for 96 hours for all species except cladocerans, which lasted 48 hours, and LC50 values were calculated as the response variable.

Chronic tests lasted for 32 days for fathead minnows and nine days for cladocerans. These tests were done according to procedures similar to those described by ASTM (1983) and Mount and Norberg (1982), respectively. Survival, growth and/or reproduction were used as the response variable in these tests. All animals obtained from outside sources were held in the dilution water for at least two weeks before testing. During the holding period, fish were treated for disease, if needed, according to procedures described by ASTM (1980).

Statistical analysis

The computerized, modified, trimmed Spearman-Karber method described by Hamilton et al. (1977) was used to determine 48- and 96-h LC50 values. Daily mortality data of replicate exposure tanks were combined before LC50 values were calculated.

For chronic tests, survival and embryo hatchability data were transformed to arcsin % (Dixon and Massey, 1957) for variance stabilization. Individual weights from fish in replicate chambers were pooled before the data was subjected to a one way analysis of variance (P = 0.05) and to Dunnett's one-sided comparison of treatment means to control means (P = 0.05) (Steel and Torrie, 1960).

RESULTS

Water parameters measured for tests conducted monthly in St. Louis River, reconstituted, and Lake Superior water are shown in Table 2. Dissolved oxygen concentrations in all tests were maintained between 60 and 100% of saturation. Tests were not continued with reconstituted water during the months of November and December because of unexplained mortality of animals cultured in this water during October. Lake Superior water was used to replace reconstituted water as a representative of laboratory water in the months of November and December.

No particular trend was observed for any water quality parameter w th time and most values were relatively constant [<25% relative standard deviation (RSD)]. Values for turbidity and dissolved solids, however, were highly variable (100 and 129% RSD, respectively).

Monthly LC50 values for tests with one-day-old fathead minnows exposed to cadmium in St. Louis River and reconstituted water are shown in Figure 4. The mean acute value for cadmium obtained from Lake Superior water tests in November and December was 42 µg/l. Acute values calculated from exposures in river water varied by a factor of three, whereas values obtained from tests conducted in reconstituted and Lake Superior water varied by less than a factor of two. The average acute values for St. Louis River water were approximately five and two times higher than those obtained for reconstituted and Lake Superior water, respectively. Linear regression correlation coefficients obtained for acute toxicity and seasonal water quality parameters are shown in Table 3. Values ranged from R = 0.21 for pH to 0.77 for dissolved solids. Correlations between acute LC50 values for fathead minnows exposed in St. Louis River and reconstituted waters on a monthly basis were significant (R = 0.75), indicating that there may have been slight

Table 2. Monthly averages in water quality parameters for cadmium tests with fathead minnows conducted in St. Louis River, reconstituted and Lake Superior water.

Parameter	April	May	June	July	August	Sept	Oct	Nov	Dec
				St. Louis River Water					
Hardness	63.0	55.0	59.0	66.0	65.0	74.0	79.0	62.0	60.0
Acidity	2.9	2.6	4.0	2.3	4.2	3.6	2.0	2.9	3.7
Alkalinity	54.0	41.0	50.0	55.0	52.0	65.0	42.0	46.0	49.0
pH	7.6	7.2	7.4	7.6	7.3	7.8	7.6	7.3	7.4
Conductivity	146	104	134	138	155	165	115	129	132
TC	-[a]	24.0	31.7	33.2	34.7	28.7	31.7	28.2	28.9
TIC	-	7.5	12.7	11.1	11.7	14.2	10.3	10.1	9.9
DIC	-	-	12.5	11.0	6.6	14.3	9.2	10.3	-
TOC	-	16.5	19.0	22.2	23.0	14.6	21.4	18.1	19.0
DOC	-	-	18.8	22.6	24.4	14.0	22.8	18.6	-
Turbidity	3.0	2.0	6.0	20.0	10.0	3.0	5.0	2.0	2.0
Color (CU)	120	150	190	230	210	180	280	195	120
CL-	6.5	5.0	4.0	4.5	5.0	5.5	6.0	5.0	5.0
SO_4^{2-}	11.0	10.0	9.0	10.0	15.0	12.0	12.0	18.0	13.0
Susp. Solids	6.8	2.8	9.2	27.0	14.4	0.4	0.4	0.4	1.2
Diss. Solids	97	104	104	142	147	144	114	136	125
				Reconstituted Water					
Hardness	40.0	48.0	41.0	42.0	41.0	39.0	-	-	-
Alkalinity	30.0	42.0	29.0	30.0	29.0	26.0	-	-	-
Acidity	-	2.1	2.3	1.9	5.7	4.1	-	-	-
pH	7.5	7.9	7.'	7.3	7.0	7.7	-	-	-
Conductivity	136	155	167	165	136	160	-	-	-
				Lake Superior Water					
Hardness	-	45.0	-	-	-	-	-	47.0	44.0
Alkalinity	-	40.0	-	-	-	-	-	42.0	41.0
Acidity	-	2.1	-	-	-	-	-	2.2	3.4
pH	-	7.4	-	-	-	-	-	7.4	7.4
Conductivity	-	100	-	-	-	-	-	95.0	9.30

[a] No measurement made

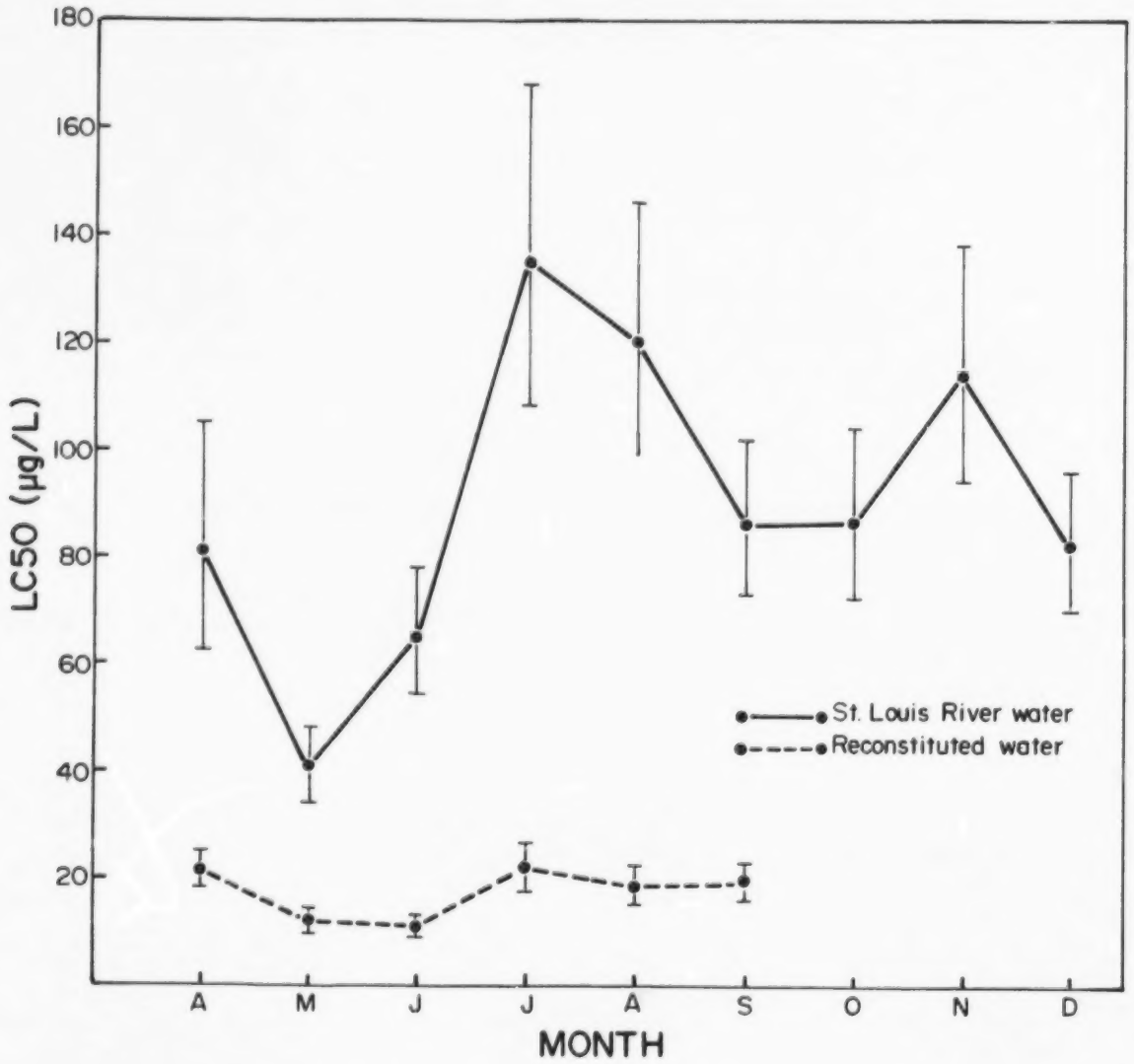

Figure 4. Monthly LC50 values (±95% confidence limits) for tests with one-day-old fathead minnows exposed to cadmium in St. Louis River and reconstituted water.

Table 3. Correlation coefficients for St. Louis River cadmium toxicity tests with fathead minnows and corresponding water quality parameters for the months April through December 1981.

Water quality parameter	Linear regression correlation coefficient
Hardness	0.34
Alkalinity	0.34
pH	0.21
Total organic carbon	0.60
Turbidity	0.68
Suspended solids	0.58
Dissolved solids	0.77

differences in the sensitivity of various batches of fish over time. All fathead minnows were obtained from the same culture unit at our laboratory throughout the testing period.

Acute values for 12 species of aquatic species exposed to St. Louis River and reconstituted water are shown in Table 4. Comparative data showed that cadmium was less toxic to four out of five species in St. Louis River water than it was in reconstituted water. Values for G. pseudolimnaeus were nearly the same in both waters, resulting in a water effect ratio (relating LC50 values in river water over those in reconstituted water) of one. It is not clear why this species responded differently than the others; however, this test may reflect very little or no difference in cadmium binding capacity in the test waters at the time of sampling. Water effect ratios for fathead minnows, cladocerans (S. serrulatus), rainbow trout and brown trout ranged from 2.6 to 10.8.

Chronic effects of cadmium on fathead minnows exposed in St. Louis River water are presented in Table 5. Cadmium significantly reduced embryo hatchability and survival and caused larval deformity at concentrations of 51.6 and 98.3 µg/l. All larvae exposed to 98.3 µg/l were dead immediately after hatch and only 13% remained alive after this period at 51.6 µg/l. After four days post hatch, survival of larvae exposed to the next lower concentration of 26.7 µg/l was reduced to 60%. Mortality continued at this concentration throughout the test period, resulting in a significant reduction in survival by the end of the 32-day test. Significant reductions in survival were not observed in fish exposed to 13.4 µg/l and below. Growth was not decreased at any of the concentrations where fish survived. Based on these results, the upper chronic limit (lowest tested concentration which caused significant decreases from the control) for cadmium in St. Louis River

Table 4. Acute values (LC50, µg/l) for aquatic species exposed to cadmium in St. Louis River and reconstituted water.

Species	Endpoint	Exposure Water	
		St. Louis River	Reconstituted
Daphnia magna	48-h	166 (124-221)	-[a]
Ceriodaphnia reticulata	48-h	129 (104-160)	
Simocephalus vetulus	48-h	89.3 (73.6-108)	-
Simocephalus serrulatus	48-h	123 (106-141)	24.5 (18.6-32.1)
Gammarus pseudolimnaeus	48-h	54.4 (35.7-82.9)	68.3 (38.7-121)
Hyalella azteca	96-h	285 (232-350)	-
Paraleptophlebia praepedita	96-h	449 (166-1217)	-
Salmo gairdneri	96-h	10.2 (7.9-13.1)	2.3 (1.6-3.3)
Salmo trutta	96-h	15.1 -[c]	1.4 (1.1-1.8)
Pimephales promelas	96-h	3390 (2710-4240)	1280 (1100-1470)
Lepomis macrochirus	96-h	8810 (8200-9450)	-
Ictalurus punctatus	96-h	7940 (7080-8910)	-

[a] No test was conducted
[b] 95% confidence limits
[c] 95% confidence limits could not be calculated using this method

Table 5. Survival and growth of fathead minnows exposed to various concentrations of cadmium in St. Louis River water for 32 days.

Measured water concentration (µg/l)	Embryo hatchability (%)	Normal larvae at hatch (%)	Survival (%)	Mean weight (mg)
<0.25 (control)	100 ± 0.0	100 ± 0.0	93 ± 0.0	107 ± 24(28)[b]
6.4 ± 0.7[a](9)[b]	97 ± 4.9	97 ± 4.9	94 ± 9.2	110 ± 20(28)
13.4 ± 1.8(9)	100 ± 0.0	100 ± 0.0	94 ± 9.2	103 ± 30(28)
26.7 ± 3.1(9)	97 ± 4.9	97 ± 4.9	30 ± 4.2*	105 ± 47(9)
51.6 ± 1.5(3)	73 ± 0*	0*	0*	-
98.3 ± 3.8(2)	83 ± 14*	0*	0*	-

[a] mean ± standard deviation

[b] number of fish weighed

* asterisk denotes values significantly different from the controls (P = 0.05)

water was 26.7 µg/l and the lower chronic limit (the highest tested concentration which did not cause significant decreases from the control) was 13.4 µg/l. The chronic value (geometric mean of the chronic limits) for this species was 18.9 µg/l.

Chronic effects of cadmium on cladocerans (Ceriodaphnia reticulata) exposed in St. Louis River water are shown in Table 6. After six days of exposure, survival of daphnids was reduced to 30% at 15.2 µg/l. Only one animal remained alive (10%) at this concentration by the end of the nine-day test. Young production occurred at all concentrations after six days of exposure. However, the mean number of young produced was significantly reduced after six days at 15.2 µg/l and nine days at 7.2 µg/l. The chronic value for this species based on the chronic limits of 3.4-7.2 µg/l calculated from these results was 4.9 µg/l.

Table 6. Survival and young production of Ceriodaphnia reticulata exposed to various cadmium concentrations in St. Louis River water for 9 days.

Measured water concentration (ug/l)	Survival (%)	Mean number of young
<0.25 (control)	80 ± 42	5.2 ± 5.3
0.9 ± 0.1[a]	90 ± 32	4.0 ± 3.6
1.8 ± 0.2	80 ± 42	3.8 ± 1.8
3.4 ± 0.2	80 ± 42	2.4 ± 2.5
7.2 ± 0.6	60 ± 52	2.1 ± 2.0*
15.2 ± 0.6	10 ± 32*	0.4 ± 1.0*

[a] mean and standard deviation of four samples

* asterisk denotes values significantly different from the control (P = 0.05)

DISCUSSION

Seasonality (96-h) acute tests with one-day-old fathead minnows conducted in St. Louis River water indicated that cadmium toxicity was significantly correlated to turbidity and dissolved solids concentration in the water. The LC50 values varied by more than a factor of three and increased with increased turbidity and dissolved solids concentration. The variation in LC50 values for tests conducted in reconstituted water was less than a factor of two. The larger variation in values obtained from tests conducted in site water was attributed to high and low stream flows which influenced turbidity and dissolved solids concentrations throughout the year. The direct proportionality found between toxicity and these parameters suggests that the large degree of binding or complexing of cadmium that occurred during times when concentrations of particulates in this water were the highest resulted in reduced cadmium toxicity. Although this effect on toxicity was not dramatic in the present tests, larger variations in toxicity may occur in streams where particulate loads change significantly during different times of the year. The frequency of testing needed to determine seasonal toxicity differences will depend on this variability. The frequency will have to coincide with the waste treatment facilities design flow or with NPDES permits issuance.

The acute toxicity tests demonstrated that cadmium was less toxic in St. Louis River water than in reconstituted or Lake Superior water. The difference was observed in seasonality tests with fathead minnow larvae and in tests utilizing juveniles of five species including both invertebrates and fish. These findings indicate that physical and/or chemical characteristics of the St. Louis River water reduced the biological availability and/or toxicity of cadmium from that observed in reconstituted or Lake Superior

water. This result confirms the basic assumption underlying the indicator species approach for criteria modification which this study was designed to verify in a field situation. Although certain factors such as pH, hardness, alkalinity and carbon dioxide have been the most studied and quantified with respect to their effects on heavy metal toxicity, the literature indicates that organic solutes, inorganic and organic colloids, and suspended particulates play a major role in affecting the toxicity of heavy metals to aquatic life (Spoor, personal communication). Recent work by Benoit (personal communication) has shown that hardness alone has relatively no effect on cadmium toxicity in Lake Superior water, but that suspended solids (clay) and dissolved solids (humic acid) greatly reduce cadmium toxicity to fathead minnows.

CRITERIA CALCULATION

Based on the results of the tests described above, site-specific, water quality criteria for cadmium in the St. Louis River were derived using the following procedures.

Recalculation procedure

This procedure allows for modification of the national maximum concentration, by eliminating data for non-resident species from the national data base.

Values for the minimum data set for cadmium from the national criteria document for species and families resident to this site are provided in Appendix C. These data were sufficient to meet the minimum data set requirements of the National Guidelines (U.S. EPA, 1983a). No additional acute tests in laboratory water were needed to calculate a site-specific, criterion using this procedure. The Species Mean Acute Values (SMAV's) are listed in order of the highest to the lowest. Family Mean Acute Values (FMAV's) are similarily listed and were used to calculate the site-specific, Final Acute Value (FAV). Family Mean Acute Values differed in some cases from the SMAV's when a family was represented by more than one species.

The site-specific, FAV for this procedure and cadmium was calculated to be 2.4 µg/l. The site-specific, maximum concentration was derived by the following equation:

$$\text{Site-Specific, Maximum Concentration} = \frac{\text{Site-Specific, Final Acute Value}}{2}$$

Because the toxicity of cadmium has been related to the hardness of the water, this relationship was taken into account before the site-specific, maximum concentration was calculated. The site-specific, maximum concentration for cadmium from the above equation, adjusted for hardness of the St. Louis River (~55 mg/l as $CaCO_3$; the lowest hardness measured in this water over a years' time) was 1.3 µg/l using the recalculatior procedure (Appendix C).

No testing was required to determine a site-specific, 30-day average concentration using this procedure. A site-specific, Final Chronic Value (FCV) can be derived from this procedure by dividing the site-specific, FAV by the national acute-chronic ratio. Since the national acute-chronic ratio for cadmium is 2.0 (U.S. EPA, 1983d), the site-specific, FCV for cadmium is the same as the site-specific, maximum concentration, 1.3 µg/l. Since a site-specific, Final Residue Value or a Final Plant Value was not available, the site-specific, 30-day average concentration for cadmium in St. Louis River, using the recalculation procedure, was 1.3 µg/l.

Indicator species procedure

This procedure is based on the determination of a water effect ratio to account for the differences in the toxicity of cadmium in St. Louis River and laboratory water due to physical and/or chemical characteristics of these waters. Tests for each species were conducted in each water, at the same time, and under similar test conditions. A water effect ratio was calculated as:

$$\text{Water Effect Ratio} = \frac{\text{Site Water LC50}}{\text{Lab Water LC50}}$$

Measured LC50 values for a toxicant must be significantly different in the two waters for this procedure to be valid. (If the values are not different, then the national, maximum concentration is the site-specific, maximum concentration.)

Water effect ratios were obtained from tests with several fish and invertebrate species (Appendix D). Although only tests with one fish and one invertebrate species were required for this procedure, tests were conducted with several species to provide additional information for this study. A filter feeder (cladoceran) was included because it is one of the most sensitive species to cadmium in the national criteria document. Because it ingests particulate matter for food, this type of species also provided a good example to discern differences in the biological availability and/or toxicity for cadmium. Two species of trout, fathead minnows, and amphipods were also tested because they are examples of both cold and warm water species and are dissimilar taxonomically.

The results of these tests indicated that cadmium was generally less toxic in site water than in reconstituted water. An exception to this occurred in tests with amphipods where the toxicity of cadmium was the same in both waters, resulting in a water effect ratio of 1.0. Tests with brown trout, on the other hand, showed that there was a large toxicity difference resulting in a water effect ratio of 10.2. Since these ratios were statistically different from water effect ratios obtained for the other species, they were not used in the calculation of a site-specific, maximum concentration for the purposes of this study. If water effect ratios from tests with only these two species were available, additional tests would have been needed to confirm or refute the differences in ratios found between these species.

The 96-h LC50 values for cladocerans, rainbow trout and fathead minnows were statistically different in both site and laboratory water and their water effect ratios were similar, allowing them to be used for the calculation of a site-specific, maximum concentration in the following equation:

Site-Specific, Maximum Concentration (7.0 µg/l)	=	Geometric Mean Water Effect Ratio (3.9)	x	National, Maximum Concentration (1.8 µg/l)

The national, maximum concentration of 1.8 µg/l was adjusted for the hardness of the laboratory water (45 mg/l as $CaCO_3$) before the site-specific, maximum concentration was calculated. The site-specific, maximum concentration for cadmium for the St. Louis River was 7.0 µg/l using the indicator species procedure.

The site-specific, 30-day average concentration for the indicator species procedure can be derived by 1) calculation (no testing required) using the national acute-chronic ratio and applying it to the site-specific, FAV, by 2) performing two pairs of acute and chronic tests which include tests with both a fish and an invertebrate species conducted in site water and by applying the resulting acute-chronic ratio to the site-specific, FAV, and by 3) conducting chronic tests with both a fish and an invertebrate species in site and laboratory water and then applying the chronic water effect ratio to the national FCV.

Since the national acute-chronic ratio for cadmium is 2.0 the site-specific, 30-day average concentration using the first method was the same as the site-specific, maximum concentration of 7.0 µg/l. The following equation was used for the calculation:

$$\text{Site-Specific, Final Chronic Value} = \frac{\text{Site-Specific, Final Acute Value}}{\text{National Final Acute-Chronic Ratio}}$$

The site-specific, 30-day average concentration using the second method was calculated to be 0.3 µg/l based on a geometric mean acute-chronic ratio of 50 (from present tests performed in the St. Louis River water, Appendix E) and the following equation:

$$\text{Site-Specific, Final Chronic Value} = \frac{\text{Site-Specific, Final Acute Value}}{\text{Site-Specific, Final Acute-Chronic Ratio}}$$

The site-specific, chronic value was obtained for both of these methods by using a site-specific, FAV of 14 (two times the site-specific, maximum concentration obtained from this procedure).

Although tests were not conducted specifically to obtain a site-specific, chronic value using the third method, due to the time constraints of this study, comparisons were made between present chronic tests in St. Louis River water and recent tests conducted with the same species in Lake Superior water at the Environmental Research Laboratory-Duluth, Duluth, Minnesota for use as an example for providing a chronic water effect ratio for this method (Appendix F). The mean, chronic, water effect ratio from these studies for two species (fathead minnows and cladocerans) was determined to be 1.0 because the chronic values obtained from tests in site and laboratory water were not significantly different (the chronic limits overlapped) (U.S. EPA, 1983b). Since the mean, chronic, water effect ratio was not different from

1.0, the site-specific, FCV is the same as the national FCV adjusted for the hardness of the St. Louis River or 2.2 µg/l using this method (Appendix H).

Resident species procedure

This procedure allowed for modification of the cadmium national criteria on the basis of tests conducted in site water with a set of species resident in St. Louis River (Appendix G). Because the minimum data set requirements for resident species were met at the St. Louis River site, substitute families were not needed for testing under this procedure. Furthermore, a family in a phylum other than arthropoda or chordata (i.e. Rotifera, Annelida, Molluska, etc.), was not included in this data set because it was not a requirement of the National Guidelines at the time that these tests were conducted.

The site-specific, FAV calculated using the prescribed method (U.S. EPA, 1983a) for resident species was 3.8 µg/l. The site-specific, maximum concentration was calculated as:

$$\text{Site-Specific, Maximum Concentration} = \frac{\text{Site-Specific, Final Acute Value}}{2}$$

The resulting site-specific, maximum concentration for cadmium using the resident species procedure was 1.9 µg/l.

The 30-day average concentrations for the resident species procedure were obtained by the same methods (1 and 2) described earlier under the indicator species procedure using 3.8 µg/l as the site-specific FAV. The site-specific FCV's for these methods were 1.9 and 0.1 µg/l, respectively. The third method was the same as that for the indicator species procedure and resulted in a site-specific FCV of 2.2 µg/l (Appendix H).

Summary of criteria calculation

Cadmium water quality criteria derived from the national and site-specific procedures are compared in Appendix H. Criteria derived from the recalculation procedure were slightly lower than those of the national criteria. The lower recalculated criteria were attributed to the lower number of families used to calculate the site-specific FAV's (10 as compared to 21) and to the use of the same sensitive families in both procedures. The maximum concentration criterion obtained from this procedure will usually be lower than national value because the smaller "N" is, the lower the FAV will be (National Guidelines, U.S. EPA, 1983a). Site-specific criteria for cadmium derived from the indicator species procedure were higher than those derived from the national and the recalculation procedure. This result was expected because criteria derived from this procedure were based on a water effect ratio which was attributed to site water characterisitics that decreased the bioavailability and/or toxicity of cadmium. Cadmium was found to be less toxic to several species in St. Louis River water than in laboratory water. The site-specific, maximum concentration derived from the resident species procedure was slightly higher than the criterion derived from the recalculation procedure but less than that obtained from the indicator species procedure. This result was also expected and attributed to the combination of using a limited data base (N = 8) (which resulted in a lower criteria) and the use of site water tests (which resulted in higher criteria due to the mitigating effects of the site water characteristics). In addition, the site-specific, 30-day average concentrations derived from the chronic, water effect ratio method in the present example were the same as the national FCV (adjusted for the hardness of our laboratory water) because the mean, chronic water effect ratio was not significantly different from

1.0. The low, 30-day average concentration obtained from the second method of both the indicator and resident species procedures was attributed to the large, site-specific, acute-chronic ratio used in the calculation of the site specific FCV. The large acute-chronic ratio obtained from the present tests was obtained for commonly tested species (one fish and one invertebrate) which were different from the species used to calculate the national Final Acute-Chronic Ratio of 2.0. The low acute-chronic ratio used in the national water quality criteria document for cadmium (U.S. EPA, 1983d) was determined for chinook salmon. Because the Final Acute Value for cadmium was based on rainbow trout, a species in the same family as the chinook salmon, higher ratios were not used.

OVERALL ASSESSMENT

Although all of the above procedures were tested in this study, only one of these approaches would most likely be used in an actual site criteria modification. If species sensitivity was the important factor, the recalculation procedure would be the least costly approach because it would require no testing. When water quality at a site may mitigate the toxicity of a chemical, the indicator species procedure is encouraged. This is especially true for metals like cadmium where biological availability and/or toxicity are significantly effected by variations in water quality characteristics of the site water. When both species sensitivity and water quality are important considerations for a particular site, the resident species procedure would be the best approach because it is designed to account for differences due to both of these factors. This approach, however, would be the most costly because at least eight acute tests are required to be conducted in site water.

The above procedures were designed for deriving site-specific water quality criteria by allowing substantial flexibility with respect to the methodology used. This should permit regulatory agencies to choose the most efficient means of obtaining the information needed to modify national criteria for each particular site. Site-specific, water quality criteria for cadmium and the St. Louis River obtained from the site specific guidelines appear to be logical, taking into account the national cadmium criteria and physical, chemical and biological characteristics of this site water. Using these procedures to derive site-specific water quality criteria for toxic materials at different sites should provide additional input to the development of effective, site-specific guidelines.

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Appendix A. Biological survey of aquatic species resident to the St. Louis River and river basin.

PLANKTON

PHYTOPLANKTON

Bacillariophyceae (diatoms)

Achnanthes lanceolata var. rostrata
Asterionella formosa
Cocconeis spp.
Coscinodiscus spp.
Cyclotella meneghiniana
Cymbella spp.
Diatoma himenale
Diatoma spp.
Eunotia pectinalis
Fragilaria capucina
Fragilaria crotonensis
Fragilaria spp.
Gomphonema spp.
Melosira distans
Melosira granulata
Melosira varians
Melosira spp.
Meridion circulare
Navicula cuspidata
Navicula exigua
Navicula gastrum
Navicula hungarica
Navicula pupula
Navicula radiosa
Navicula viridula
Navicula spp.
Nitzschia palea
Nitzschia tryblionella
Nitzschia spp.
Pinnularia spp.
Rhoicosphenia curvata
Stauroneis crucicula
Stephanodiscus spp.
Synedra actinastroides
Synedra ulna
Synedra spp.
Tabellaria fenestrata
unidentified diatoms

Chlorophyta (green algae)

Actinastrum spp.
Ankistrodesmus
Cosmarium
Crucigenia quadrata
Elaktothrix viridis
Kirchneriella lunaris
Pandorina morum
Pediastrum duplex
Scenedesmus spp.
unidentified unicells
unidentified colonies
unidentified filaments

Cyanophyta (blue-green algae)

Anabaena spp.
Anacystis spp.
Aphanocapsa spp.

Euglenophyta

Euglena spp.
Phacus longicauda

Pyrrophyta

Ceratium hirudinella

Cryptomonadales

Cryptomonas erosa

Appendix A. (Continued)

ROTOTARIA

Conochilus sp.
Synchaeta sp.
Keratella cochlearis
Keratella quadrata
Kellicottia longispina
Polyarthra sp.
Agplanchia priodonta
Pleosoma hudsonia
Brachionus sp.
Cupelopagis sp.
Tetramastix sp.
Trichocerca sp.
Filinia sp.
Monostyla sp.

ZOOPLANKTON

Cladocera

Ceriodaphnia megalops
Ceriodaphnia reticulata
Simocephalus vetulus
Simocephalus serrulatus
Eubosmina coregoni
Bosmina longirostris
Bosmina coregoni
Daphnia pulex
Daphnia retrocurva
Daphnia ambigua
Daphnia galeata mendotae
Leptodora kindtii
Diaphanosoma birgei
Alona guttata
Alona sp.
Chydorus sp.
Latona setifera
Camptocercus sp.
Pleuroxus sp.
Sida sp.

Copepoda

Diaptomus ashlandi
Diaptomus sicilis
Diaptomus minutes
Diaptomus oregonensis
Diaptomid copepodids
Eurytemora affinis
Epischura lacustris
Limnocalnus macrurus
Leptodiaptomis minutus
Leptodiaptomus sicilis
Leptodiaptomis siciloides
Leptodiaptomus ashlandi
Epischura lacustris
Skistodiaptomus oregonensis
Cyclopoid copepodids
Cyclops bicuspidatus
Cyclops vernalis
Eucyclops agilis
Mesocyclops leukarti
Mesocyclops edax
Paracyclops fimbriatus
Diacyclops thomasi
Macrocyclops albidis
Acanthocyclops vernalis
Tropocyclops prasinus
Halocyclops sp.
Orthocyclops modestus
Harpacticoida sp.
Osphranticum sp.

Appendix A. (Continued)

BENTHIC ORGANISMS

ANNELIDA

- Oligochaeta
  - Tubifex sp.
- Polychaeta
  - Helobdella stagnalis
  - Helobdella elongata
  - Manayunkia sp.
- Hirudinae
  - Illinobdella alba

MOLLUSCA

- Pelecypoda
  - Sphaerium transversum
  - Sphaerium simili
  - Sphaerium lacustra
  - Sphaerium nitidium
  - Sphaerium securis
  - Sphaerium partumium
  - Sphaerium rhomboideum
  - Sphaerium favale
  - Sphaerium striatinum
  - Sphaerium occidintale
  - Pisidium fallax
  - Campeloma sp.
  - Musculium sp.
- Gastropoda
  - Amnicola limnosa
  - Valvata sincera
  - Valvata tricarinata
  - Promentus exacuous megas
  - Promentus unbilicatellus
  - Gyraulus deflectus
  - Helisoma anceps
  - Physa sp.

ANTRHOPODA

- Amphipoda
  - Gammarus pseudolimnaeus
  - Gammarus fasciatus
  - Gammarus lacustris
  - Hyalella azteca
  - Pontoporeia affinis
- Isopoda
  - Asellus intermedius
  - Asellus racovitzae
- Ephemoroptera
  - Paraleptophlebia praepedita
  - Hexagenia sp.
  - Caenis sp.
  - Ephemerella sp.
- Tricoptera
  - Phylocentropis sp.
  - Oecetis sp.
  - Glossosoma sp.
  - Neureclipsis sp.
  - Molanna sp.
  - Leptocella sp.
  - Wormaldia sp.
- Diptera
  - Microspecta sp.
  - Tribelos sp.
  - Chaoborus sp.
  - Cricotopus sp.
  - Procladius sp.
  - Parachironomus sp.
  - Cryptochironomus sylifera
  - Cryptochironomus nais
  - Xenochironomus sp.
  - Chironomus sp.
  - Polypedilum sp.
  - Clinotanypus sp.
  - Coelotanypus sp.
  - Ablabesmyia sp.
  - Glyptotendipes sp.
  - Tanytarsus sp.
  - Palpomia sp.

Appendix A. (Continued)

FISH

Pètromyzontidae
- Silver lamprey (Ichthyomyzon unicuspis)

Anguillidae
- American eel (Anguilla rostrata)

Clupeidae
- Alewife (Alosa pseudoharengus)

Salmonidae
- Pink salmon (Oncorhynchus gorbuscha)
- Chinook salmon (Oncorhynchus tshawytscha)
- Rainbow trout (Salmo gairdneri)
- Brown trout (Salmo trutta)
- Lake herring (Coregonus artedi)

Osmeridae
- Rainbow smelt (Osmerus mordax)

Umbridae
- Central mudminnow (Umbra limi)

Esocidae
- Northern pike (Esox lucius)
- Muskellunge (Esox masquinongy)

Cyprinidae
- Lake chub (Couesius plumbeus)
- Creek chub (Semotilus atromaculatus)
- Carp (Cyprinus carpio)
- Goldfish (Carassius auratus)
- Golden shiner (Notemigonus crysoleucas)
- Emerald shiner (Notropis atherinoides)
- Common shiner (Notropis cornutus)
- Spottail shiner (Notropis hudsonius)
- Mimic shiner (Notropis volucellus)
- Fathead minnow (Pimephales promelas)
- Bluntnose minnow (Pimephales notatus)
- Longnose dace (Rhinichthys cataractae)

Catostomidae
- Longnose sucker (Catostomus catostomus)
- White sucker (Catostomus commersoni)
- Silver redhorse (Moxostoma anisurum)
- Shorthead redhorse (Moxostoma macrolepidotum)

Appendix A. (Continued)

Ictaluridae
- Black bullhead (Ictalurus melas)
- Yellow bullhead (Ictalurus natalis)
- Brown bullhead (Ictalurus nebulosus)
- Channel catfish (Ictalurus punctatus)
- Stonecat (Noturus flavus)
- Tadpole madtom (Noturus gyrinus)

Percopsidae
- Trout-perch (Percopsis omiscomaycus)

Gadidae
- Burbot (Lota lota)

Gasterosteidae
- Brook stickleback (Culaea inconstans)

Percichthydae
- White bass (Morone chrysops)

Centrarchidae
- Rock bass (Ambloplites rupestris)
- Pumpkinseed (Lepomis gibbosus)
- Bluegill (Lepomis macrochirus)
- Smallmouth bass (Micropterus dolomieui)
- White crappie (Pomoxis annularis)
- Black crappie (Pomoxis nigromaculatus)

Percidae
- Johnny darter (Etheostoma nigrum)
- Yellow perch (Perca flavescens)
- Logperch (Percina caprodes)
- Walleye (Stizostedion vitreum vitreum)

Sciaenidae
- Freshwater drum (Aplodinotus grunniens)

Appendix B. Ambient water quality parameters obtained for the St. Louis River site at Cloquet, Minnesota during the months of April through December 1981[a].

Date	Water Depth	Water Temp (°C)	DO (mg/1)	pH	T Alk $CaCO_3$ (mg/1)	Turb Trbid Mtr Hach FTU	Color Pt-CO Units	BOD 5-day (mg/1)	COD Low Level (mg/1)	Phos-Tot (mg/1)	Tot Kjel N (mg/1)
81/04/14	50	6	9.9	7.9	39	6.0	140	2.0	40	0.056	0.99
81/05/13	05	12	8.5	7.7	31	6.0	200	2.0	52	0.032	0.99
81/07/01	03	19	5.6	7.5	37	14.0	280	2.0	84	0.084	1.30
81/07/08	05	26	5.1	7.1	44	3.0	210	1.0	72	0.470	0.99
81/08/05	20	22	5.6	7.5	57	4.0	210	1.0	64	0.034	0.99
81/09/09	10	20	6.9	8.1	67	5.0	180	2.0	52	0.040	0.99
81/10/20	50	7	9.1	7.7	40	12.0	280	2.0	80	0.062	1.54
81/11/04	17	6	10.0	7.5	42	4.0	195	2.0	60	0.028	1.10
81/12/09	04	0	12.1	7.3	52	2.0	120	3.2	60	0.016	0.77

Date	NH_3+NH_4-N Total (mg/1)	NO_3-N Total (mg/1)	Chloride Total (mg/1)	Sulfate SO_4-Tot (mg/1)	Tot hard $CaCO_3$ (mg/1)	Residue Total (mg/1)	Residue Tot NFLT (mg/1)	Residue Diss 105 (mg/1)	Conductivity at 25°C (micromno)
81/04/14	0.04	0.22	7	12	61	138	11	127	138
81/05/13	0.02	0.09	5	12	52	134	8	126	98
81/07/01	0.04	0.10	4	9	49	170	42	128	80
81/07/08	0.01	0.10	5	10	55	-	4	-	112
81/08/05	0.02	0.13	5	12	68	170	2	168	133
81/09/09	0.10	0.05	5	11	77	163	4	159	160
81/10/20	0.03	0.09	6	12	56	164	22	142	105
81/11/04	0.02	0.12	6	13	63	146	4	142	104
81/12/09	0.03	0.20	5	12	62	131	2	129	130

Date	Copper Cu, Tot (µg/1)	Zinc Zn, Tot (µg/1)	Nickel Ni, Tot (µg/1)	Chromium Cr, Tot (µg/1)	Cadmium Cd, Tot (µg/1)
81/04/14	18	20	16	<10	<5
81/05/13	12	23	10	<10	<5
81/07/01	15	30	<10	<10	<5
81/07/08	11	27	<10	<10	<5
81/08/05	<10	18	<10	<10	<5
81/09/09	13	19	14	<10	<5
81/10/20	<10	18	10	<10	<5
81/11/04	20	20	<10	<10	<5
81/12/09	14	13	<10	<10	<5

[a] Western Lake Superior Sanitary District, Duluth, Minnesota water quality monitoring data program, SL336N.

Appendix C. RECALCULATION PROCEDURE. Minimum data set for cadmium from the national criterion document for species and families resident to the St. Louis River.

Rank	Family	Family Mean Acute Value (µg/l)	Species	Species Mean Acute Value (µg/l)
10	Bithyniidae	8,400	Snail, *Amnicola* sp.	8,400
9	Centrarchidae	3,174	Bluegill, *Lepomis macrochirus*	4,775
			Pumpkinseed, *Lepomis gibbosus*	1,343
8	Ephemerellidae	2,319	Mayfly, *Ephemerella* sp.	2,319
7	Cyprinidae	1,743	Goldfish, *Carassius auratus*	8,397
			Common carp, *Cyprinus carpio*	215
			Fathead minnow, *Pimephales promelas*	2,080
6	Chironomidae	1,200	Midge, *Chironomus* sp.	1,200
5	Anguillidae	734	American eel,[a] *Anguilla rostrata*	734
4	Physidae	150	Snail, *Physa* sp.	150
3	Gammaridae	70	Scud, *Gammarus* sp.	70
2	Daphnidae	27.8	Cladoceran, *Daphnia pulex*	40.4
			Cladoceran, *Simocephalus serrulatus*	62.3

Appendix C. (Continued)

Rank	Family	Family Mean Acute Value (µg/l)	Species	Species Mean Acute Value (µg/l)
1	Salmonidae	5.1	Chinook salmon, Oncorhynchus tswhawytscha	4.9
			Rainbow trout, Salmo gairdneri	3.9

[a] Uncommon species

Site-Specific Final Acute Value = 2.4 µg/l (calculated for a hardness of 50 mg/l from site-specific Family Mean Acute Values)

Site-Specific Criterion Maximum Concentration = (2.4 µg/l) / 2 = 1.2 µg/l (for a hardness of 50 mg/l)

ln (Site Specific Criterion Maximim Intercept = ln (1.2) - [slope x ln (50)]
= 0.182 - 4.538 = -4.356

Site-Specific Criterion Maximum Concentration = $e^{(1.16\ [\ln \text{hardness}] - 4.356}$
= 1.3 µg/l adjusted for a hardness of 55 mg/l.

Appendix D. INDICATOR SPECIES PROCEDURE. Acute values (LC50) for indicator species exposed to cadmium in St. Louis River and reconstituted water.

Species	St. Louis River Water (µg/l)	Reconstituted Water (µg/l)	Water Effect Ratio
Cladoceran (Simocephalus serrulatus)	123	24.5	5.0
Amphipod (Gammarus psuedolimnaeus)	54.5	68.3	1.0
Rainbow trout (Salmo gairdneri)	10.2	2.3	4.4
Brown trout (Salmo trutta)	15.1	1.4	10.8
Fathead minnow (Pimephales promelas)	3,390	1,280	2.6

Appendix E. Acute (LC50) and chronic values for aquatic organisms exposed to cadmium in St. Louis River water.

Species	Acute Value (µg/l)	Chronic Value (µg/l)	Acute-Chronic Ratio
Fathead minnow (Pimephales promelas)	1,830	18.9	97
Cladoceran (Ceriodaphnia reticulata)	129	5.0	26

Appendix F. Chronic toxicity values of two species exposed to cadmium in St. Louis River and Lake Superior water.

Species	Chronic Value (µg/l) St. Louis River Water	Chronic Value (µg/l) L. Superior Water	Chronic[a] Water Effect Ratio
Fathead minnow (*Pimephales promelas*)	18.9 (13-26)[b]	13[c] (9-18)	1.0
Cladoceran (*Cerodaphnia reticulata*)	5.0 (3.4-7.2)	4.2[d] (3-6)	1.0

[a] Chronic water effect ratios are 1.0 since values in site and laboratory water are not different (chronic limits overlap).
[b] Chronic limits
[c] Benoit (personal communication)
[d] Mount (personal communication)

Appendix G. RESIDENT SPECIES PROCEDURE. Minimum data set of resident aquatic species exposed to cadmium in St. Louis River water.

Rank	Species	LC50 (µg/l)
8	Bluegill (Lepomis macrochirus)	8,800
7	Channel catfish (Ictalurus punctatus)	7,900
6	Fathead minnow (Pimephales promelas)	3,390
5	Mayfly (Paraleptophlebia praepedita)	449
4	Amphipod (Hyalella azteca)	285
3	Cladoceran (Simocephalus serrulatus)	123
2	Amphipod (Gammarus psuedolimnaeus)	54.4
1	Rainbow trout (Salmo gairdneri)	10.2

Appendix H. Cadmium water quality criteria derived from the national and site specific procedures.

Criterion Derivation Procedure	Number of Families Used	Maximum Concentration (µg/l)	30-day Average Concentration (µg/l)
National	21	2.2[a]	2.2[a]
Site-Specific Recalculation	8	1.3[a]	1.3[a]
Indicator	21[b]	7.0[c]	7.0 0.3 2.2[a]
Resident	8	1.9	1.9 0.1 2.2[a]

[a] Adjusted for a water hardness of the St. Louis River of 55 mg/l as $CaCO_3$.

[b] The national data base containing 21 families was used in this calculation.

[c] A national criterion of 1.8 µg Cd/l (adjusted for a hardness of 45 mg/l hardness (as $CaCO_3$)) was used in this procedure.